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Raman and DFT Study on N-H⁺...Cl⁻ Hydrogen Bonding in 1,1,3,3-Tetra-Methylguanidinium Chloride forming an Ion-pair Molecule in the Vapor Phase

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The chemistry of 1,1,3,3-tetramethylguanidinium ([TMGH]⁺) chloride, a low temperature (molten) ionic liquid, is discussed, based on its Raman spectra associated with *ab initio* molecular orbital DFT-type quantum mechanical calculations (with 6-311+G(d,p) basis sets) on “molecules” in isolated gaseous free states without any assumed symmetry. The calculations on the monomeric [TMGH]⁺ ion and the dimeric ion pair converged to give geometries near the established crystal structure of the [TMGH]Cl salt. This salt is known to contain dimeric ion pairs of the kind [TMGH]ClCl[TMGH]¹ (Fig.1).

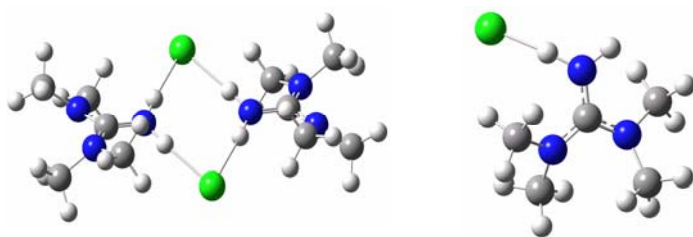
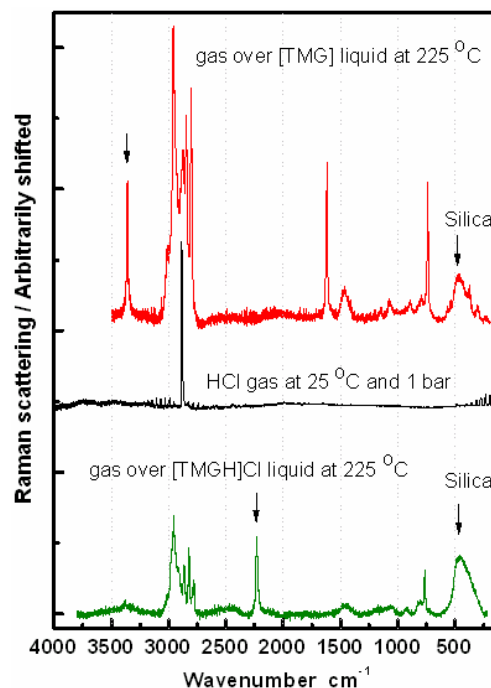


Fig.1: Solid dimeric ion pair. Fig.2. Gas molecule ion pair.

Fig. 3 Raman spectra of vapors. →

Experimentally obtained Raman scattering spectra of the compound (as the solid, as solutes in ethanolic and aqueous solutions and as a vapor at 225 °C) are presented and assigned, by comparing to the *ab initio* vibrational analyses (calculated IR and Raman band positions and intensities). It is concluded that dimeric molecular ion pairs with four N-H⁺...Cl⁻ hydrogen bonds seem to exist also in the solutions, and probably are responsible for the relatively high solubility of the “salt” in ethanol. The “salt” can be easily sublimed at about 200-230 °C. The Raman spectrum of the vapor at 225 °C has a characteristic strong band at 2229 cm⁻¹ that shows that the gas phase consists of monomeric ion pair “molecules” (Fig.2) held together by one N-H⁺...Cl⁻ hydrogen bond, the stretching band of which is causing the band² (Fig.3).



1. A. K. Fischer, P. G.; Jones, “Tetramethylguanidinium chloride”, Acta Cryst., E 58 (2002) o218-219.
2. R. W. Berg, A. Riisager and R. Fehrmann, “On the constitution of a vapor over an ionic liquid: Raman spectra of 1,1,3,3-Tetramethylguanidinium chloride in the solid state, in solution and in the vapor phase”, J. Phys. Chem. A, manuscript submitted.